Surface Freezing of Triacontane at SiO$_x$/Air Interfaces: Submonolayer Coverage

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The topology and molecular ordering of submonolayer triacontane films at SiO$_x$/air interfaces has been investigated near the bulk melting temperature. Island regions, about an extended monolayer thicker than the neighboring regions, are observed by surface force microscopy and these regions continue to exist above the bulk melting transition. X-ray reflectivity and grazing incidence angle diffraction confirm the surface freezing behavior of the alkanes. The melting temperature of the solid monolayer regions seems to coincide with the wetting transition temperature observed in samples with higher coverage. The diffraction data also reveal that the triacontane in the monolayer regions exhibits long-range order at temperatures above the bulk melting temperature, consistent with a rotator phase.

Introduction

It is well established that *n*-alkanes, with chain lengths between 15 and 50 carbon atoms, exhibit surface freezing whereby a frozen monolayer phase exists between the molten bulk and the air interface over a temperature range of up to 3 °C.[1–18] Likewise, there have also been strong indications for surface freezing of alkanes at the alkane/solid interface.[19,20] Originally this surface freezing at the alkane/solid interface was deduced from the wetting behavior of alkane melts on the SiO$_x$/air interfaces (SiO$_x$ = Si wafers with an oxide surface) which revealed a temperature-induced wetting transition between complete and partial wetting of the liquid alkane melt. It was found that the temperature of this wetting transition is very similar to the surface freezing temperature of alkane melts. The idea that alkane surface freezing also occurs at solid/vapor interfaces was corroborated by small-angle X-ray reflectivity data for samples with alkane coverages greater than a monolayer. In the proposed surface freezing temperature regime, the alkane monolayer at the SiO$_x$/air interface had approximately the thickness of one all-trans alkane chain length. In the temperature range between the wetting transition and bulk melting—the surface freezing regime—this monolayer coexists with liquid bulk droplets. This monolayer at the solid/air interface corresponds to the frozen alkane monolayer at the interface between an alkane melt and air in "conventional" surface freezing. In both cases a monolayer of solid alkane coexists at thermal equilibrium with bulk liquid alkane. For films greater than a monolayer, X-ray diffraction studies revealed that far below the surface freezing regime the alkane molecules in the monolayer at the SiO$_x$/air interface are oriented normal to the interface in an orthorhombic packing[20] similar to the bulk. In the case of "submonolayer coverage", depending on the coverage, the alkanes form a monomolecular film with holes in it or aggregate into domains with fractal shape.[20] For these films, the same overall packing arrangement is observed with the X-ray measurements as with the thicker films. Although there is indirect evidence that these films exhibit surface freezing, to date there has been no direct structural evidence.

In this paper we present convincing evidence for a solid, molecularly thick alkane film at the SiO$_x$/air interface at temperatures above the bulk melting temperatures, thus confirming the existence of surface freezing at the solid interface. We have carried out surface force microscopy (SFM), X-ray reflectivity, and X-ray diffraction measurements on samples with submonolayer coverage. Bulk alkanes (i.e., liquid or solid droplets), which might complicate the measurements and their data interpretation, are absent here. Thus, the interfacial molecular ordering can be investigated without interference from the bulk behavior.

Materials and Methods

Triacontane ("C30") with a purity of 99+% was obtained from Aldrich. Silicon wafers, obtained from WACKER SILTRONIC GmbH (Burghausen, Germany) with a natural, amorphous ≈15 Å thick oxide layer, were cut into pieces (typically 2 cm × 2 cm) for use as solid substrates. The substrate surfaces were cleaned with a modified RCA cleaning process described elsewhere (SC-1).[21] Onto these wafer surfaces ("SiO$_x$") molecularly thin alkane films were deposited by spin-coating. The overall alkane coverage could be adjusted by the alkane solution concentration

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(toluene solvent, alkane concentration typically 10^{-3} mol/L) and the rpm of the spin coating (typically between 2000 and 10000 rpm). Typically a droplet of about 50 μL was deposited on the substrate. Such a droplet contains about 3×10^{16} alkane molecules. This is sufficient for about 15 complete alkane monolayers on an area of 4 cm² if each molecule occupies an area of about 20 Å². As soon as the droplet touches the surface, it immediately spreads and completely wets the surface. Then the spin-coater is started which obviously causes a spinning off of most of the deposited solution because under these conditions typically a coverage of about one monolayer is obtained. After alkane deposition, the samples were heated to 80 °C, substantially above the bulk melting point of ≈66.9 °C and the surface freezing temperature of ≈70 °C. At 80 °C the molten alkane forms a liquid film which completely wets the surface. Subsequently the samples were cooled to room temperature. The heating/melting guarantees complete evaporation of any residual solvent and it ensures defined and reproducible starting conditions for the samples.

With this preparation procedure we were not able to prepare perfectly closed solid monolayers without holes and without any additional bulk material on top. This we attribute to the aggregation process upon solidification[20] combined with the substantial difference in the alkane density between the liquid and the solid state. Upon cooling a liquid alkane melt, with increasing alkane coverage, one finds the following topologies: (1) individual domains; (2) a contingent monolayer with holes in it; (3) a contingent monolayer with less holes in it but with some additional pieces of bulk material on top of the monolayer; and (4) a closed monolayer with lots of bulk material on it. We selected topology 2 as most suitable for our investigations because it is closest to the ideal case of a complete monolayer. Extra bulk material, whose wetting transition would interfere or hide the surface freezing transition, is absent.

The preparation and treatment of the alkane films, as well as the SFM studies and the X-ray reflectivity studies were performed under ambient air. The diffraction studies were carried out under a helium environment to minimize the effects of beam damage and to reduce the background. The SFM studies were performed in the noncontact, "tapping force" mode with a Nanoscope III (Digital Instruments, Inc., Santa Barbara, CA). For the X-ray reflectivity measurements a conventional X-ray tube source was used with a theta/theta reflectometer (STOE, Darmstadt Germany). The grazing incident angle diffraction (GID) experiments were done at Brookhaven National Laboratory beamline X22A at the National Synchrotron Light Source (NSLS, USA). The reflectivity, GID, and SFM measurements utilized different cells/sample holders. For each setup the temperature was calibrated with the bulk melting temperature of the C30. The bulk melting transition can easily be determined by visual inspection of samples with small pieces of bulk alkane because the melting of solid alkane pieces into liquid droplets changes significantly the surface reflectivity/scattering. Thus the absolute temperature calibration between different instruments is better than ±0.3 °C in the relevant temperature range. For measurements with the same instrument the temperature reproducibility was better than ±0.3 °C.

A remark on terminology: As already explained, the term "surface freezing" is commonly used to describe a *thermodynamic equilibrium configuration* where the molecules at the interface are in a solidlike, ordered state whereas the same substance in bulk forms a liquid. Surface freezing is *not* used as a phrase to describe the *process* of the solidification/crystallization ("freezing") of the interfacial molecules. Of course there is also a melting and a solidification/crystallization process of the interfacial monolayer. The corresponding temperatures differ substantially because nucleation and finite size effects lead to pronounced supercooling. In the following we will only present data obtained on heating, i.e., the melting temperature of the surface frozen alkane monolayer. Assuming no superheating, this temperature is identical to what generally is called the surface freezing temperature.

Results from SFM

Figure 1 shows SFM pictures from a sample with submonolayer alkane coverage at three different tem-
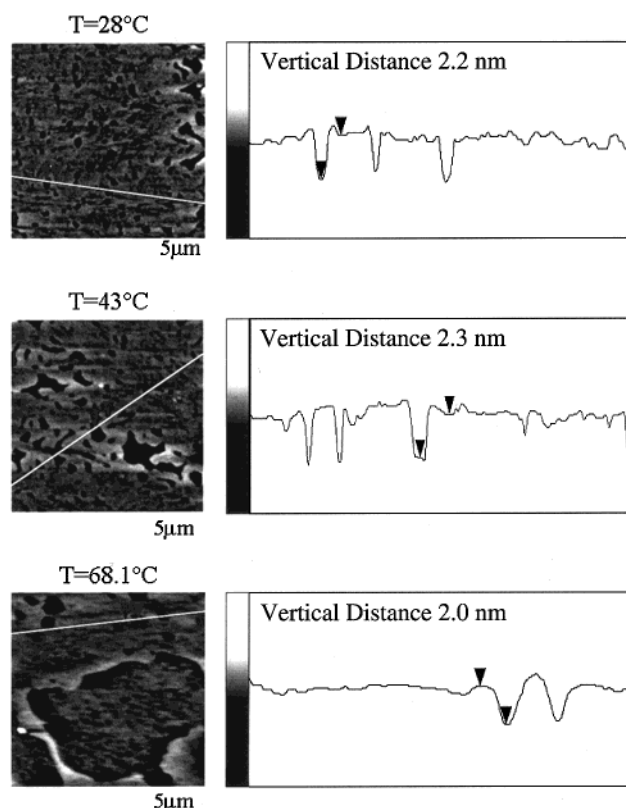

Figure 1. SFM pictures and scanning profiles of a C30 film on a SiO$_x$ surface at various temperatures. The overall coverage is ≈90% of a complete monolayer ("submonolayer coverage"). At $T = 68.1$ °C the coverage has decreased to ≈50% due to the SFM scan (see for details in the main text). The vertical depth profile is taken along the white lines as shown in the images. The brighter areas represent the alkane monolayer sections.

peratures. At 28 °C one observes a nearly complete alkane monolayer with small holes. At this temperature this surface topology is stable over many hours and not significantly affected even by multiple SFM scans of the same area. At intermediate temperatures (43 °C) the sample surface looks similar to the one at room temperature, only some of the holes appear to have increased. Multiple scanning of the same area reveals that the observed decrease of the monolayer area is largely due to the scanning procedure. With every scan some of the alkane material appears to be scratched off. At 68.1 °C still patches of alkane monolayer can be visualized. However, the holes have grown considerably in size. After only a few scans all the alkane patches have disappeared. This suggests that the alkane loss is largely due to the SFM scanning. Indeed, areas that were scanned several times will appear as regions of decreased alkane coverage within a subsequently imaged, larger surface region, with sharp boundaries between the areas that were scanned only once and those scanned repeatedly. The vertical depth profiles reveal, for all temperatures, a height difference of 20−25 Å between the top surface and the bottom of the holes. This distance is less than the length of a fully extended C30 molecule (≈41 Å).

X-ray Reflectivity Results

Figure 2 presents X-ray reflectivity data and associated fits at several temperatures. The sample exhibited an initial room temperature topology similar to that shown in Figure 1. Between room temperature and 69.5 °C the reflectivities are essentially identical. Between 69.5 and 70.3 °C they change and then remain roughly unaltered
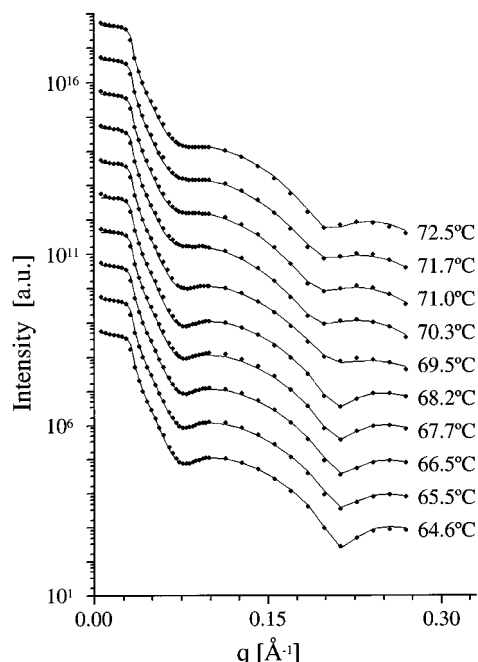
Figure 2. X-ray reflectivity data from a sample with ≈90% monolayer coverage at various temperatures. The intensities are shifted by multiples of 10 to present all reflectograms in the same figure. The dots are the measurement values; the solid lines represent best fits.
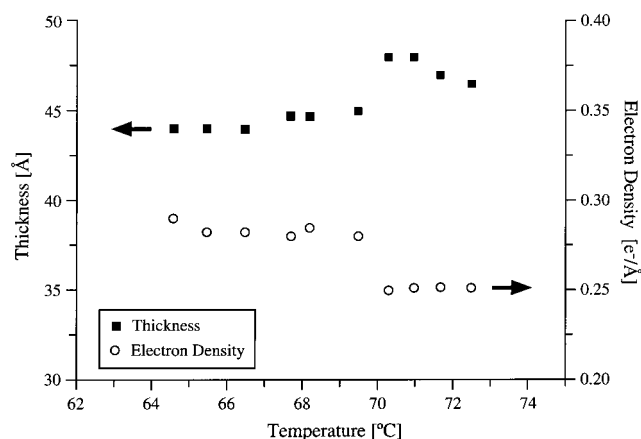
Figure 3. Thickness and electron density data derived from fits of the X-ray reflectivity measurements shown in Figure 2.

up to 72.5 °C. Figure 3 presents the film thicknesses and the electron densities derived from the fits of the curves of Figure 2. The fits assume a constant electron density for the alkane film (a single "box") with two different roughnesses at the substrate/alkane and alkane/air interfaces, respectively. The roughnesses are assumed to smoothen the edges of the "box" with Gaussian profiles (for further details on the fit procedure see ref 22). For all fits the electron density of the SiO_x substrate was kept fixed at 0.69 $e^-/Å^3$. The fits yielded interfacial roughnesses of a few angstroms, a typical value for such interfaces. The single box model does not explicitly take into account the holes in the monolayer. If these holes extend to the substrate surface, the amplitude of the observed interferences will slightly be reduced compared to monolayers without holes. That means the monolayer thickness derived from the fit will be the same as for a complete monolayer whereas the electron densities will change. If

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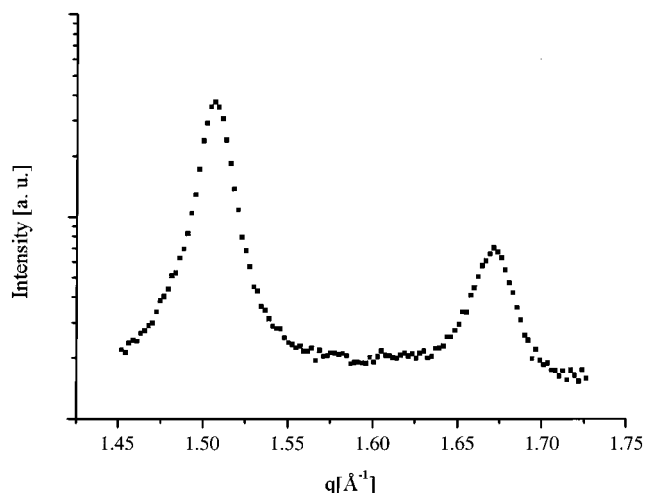
Figure 4. GID scan at room temperature with q_{xy} from 1.45 to 1.75 $Å^{-1}$ ($q_z = 0$) for a sample with nearly complete monolayer coverage similar to the one depicted in Figure 1.

the holes are partially filled with a thin alkane layer, both the amplitude and the frequency of the interference will change. Thus, the thickness and the electron density derived from a simple box model would not be the correct values for the monolayer. However, because the monolayer nearly completely covers the substrate (see Figure 1), these modifications of the reflectivity will be very weak and barely falsify the interpretation assuming a complete monolayer. Thus the holes were not taken into account. In any case, the fundamental result that the alkanes form a solid monolayer even above bulk melting is independent from details of the fitting procedure. It is obvious from the abrupt change of the reflectivity curves. Between 64.6 and 69.5 °C the thickness increases slightly from 44 to 45 Å. At 70.3 °C it increases abruptly to 47 Å. Then it decreases continuously to about 46 Å at 72.5 °C. The electron densities show a mirror−image behavior. There is a continuous decrease from ≈0.29 to 0.28 $e^-/Å^3$ at 69.5 °C, then a sharp decrease to 0.25 $e^-/Å^3$ at 70.3 °C where it remains up to 72.5 °C.

Results from X-ray Diffraction

A typical GID scan for $q_z \cong 0$ with q_{xy} ranging from 1.45 to 1.75 $Å^{-1}$, from a sample with submonolayer coverage at room temperature, is presented in Figure 4. In agreement with our previous results,[20] two peaks at $q_{xy} \approx 1.51$ $Å^{-1}$ and $q_{xy} \approx 1.67$ $Å^{-1}$ are observed. The peak maximum is at $q_z \cong 0$, thus indicating that the molecules are oriented upright. It is convenient to use a centered, rectangular unit cell to describe the diffraction. In this coordinate system the peak at 1.51 $Å^{-1}$ corresponds to the (20) reflection and the peak at 1.67 $Å^{-1}$ corresponds to the (11) reflection. Note that the (10) and (01) reflections are symmetry disallowed. It can be shown that the unit cell is 4.22 Å × 8.32 Å with an area of 35.1 $Å^2$ (two molecules) giving an area per molecule of 17.55 $Å^2$. Scans in q_{xyz} space reveal that the peak at $q_{xy} \approx 1.67$ $Å^{-1}$ disappears already substantially below the bulk melting temperature (occasionally already at ≈40 °C, some 25 °C below bulk melting!). The remaining peak is shifted to $q_{xy} \approx 1.49$ $Å^{-1}$, with its maximum still at $q_z \approx 0$. No peaks were observed off-axis, thus indicating the existence of an untilted hexagonal phase. Therefore, the disappearance of the peak at $q_{xy} \approx 1.67$ $Å^{-1}$ corresponds to a phase transition in the monolayer from a distorted, hexagonal (orthorhombic) phase to a hexagonal (rotator) phase, with the molecules oriented upright in both cases.
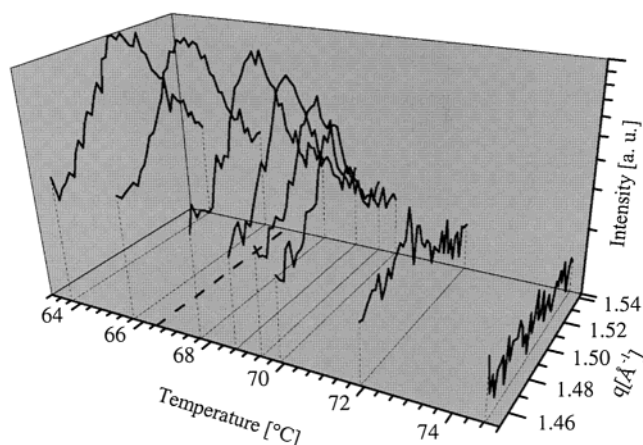
Figure 5. GID scan for a sample with nearly monolayer coverage between $q_{xy} = 1.45$ Å^{-1} and $q_{xy} = 1.55$ Å^{-1} (for $q_z = 0$) for temperatures between 64 and 75 °C. Each scan was taken from a different footprint area of the same sample. T_b indicates the bulk melting temperature.
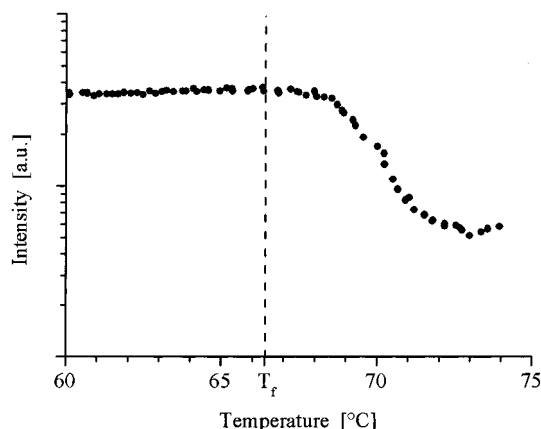
Figure 6. GID data from for a submonolayer sample obtained from the same footprint area at one fixed q_{xy} value (≈ 1.51 Å^{-1}). T_f indicates the bulk melting temperature.

To investigate the molecular ordering in the surface freezing temperature regime, the diffraction signal was monitored in the range of the hexagonal peak at $q_z = 0$ between $q_{xy} = 1.45$ Å^{-1} and $q_{xy} = 1.55$ Å^{-1} as function of the temperature. Figure 5 presents the results of such a scan for temperatures between 64 and 75 °C. The limited scanning time, less than a minute per scan, allowed us to minimize beam damage effects compared with longer, more detailed scans. Up to the bulk melting temperature at ≈ 66.9 °C, and even slightly above, the peak intensity at $q_{xy} \approx 1.49$ Å^{-1} remains approximately constant. Between 69 and 72 °C, the intensity slowly decreases, and at 75 °C the peak has disappeared completely. All of the data from Figure 5 were obtained from the same sample. To minimize radiation damage, the sample was translated for each temperature point to expose a fresh area. To further reduce possible radiation damage effects, we also carried out measurements of the diffracted intensity at a fixed position in reciprocal space ($q_{xy} \approx 1.49$ Å^{-1}) by slewing the temperature at a fixed sample position (Figure 6). The observed behavior is very similar to the one obtained from the more comprehensive measurement of the different foot print areas (Figure 5).

Discussion

The combined SFM and X-ray results provide clear proof for a solid ("frozen") molecular ordering at temperatures above the bulk melting point ("surface freezing"). The GID profiles indicate a solidlike molecular packing (Figures 4 and 5). The SFM images indeed show the existence of solid monolayer patches (Figure 1). When the alkane melts, it is not possible to image any surface topology. The loss of alkane material during the scanning at elevated temperatures close to the surface freezing point may be attributed to a transfer of alkane molecules from the planar SiO$_x$ surface to the tip which consists of the same material. This transfer is negligible at room temperature. One may speculate that the transfer is related to the monolayer phase. There seems to be a drastic increase of the loss of alkane beyond the transition to the rotator phase.

Although SFM thickness measurements with the tapping mode are inherently not very accurate, the discrepancy between the monolayer thicknesses measured by SFM ($\approx 20-25$ Å) and by X-ray reflectivity ($\approx 44-45$ Å) is significant. This discrepancy strongly suggests that the bottom of the holes in the monolayer is not the bare substrate surface. The holes may be covered with alkanes which are not standing up straight. We also note that the monolayer thickness derived from X-ray reflectivity exceeds the molecular all-trans length. This is in agreement with previous observations[19] and was attributed to strong fluctuations along the molecular axis normal to the surface in accordance with the current theory on surface freezing.[9,12,13] Indeed, such fluctuations would effectively increase the layer thickness. Recent ellipsometric measurements from the Taub group,[23] however, suggest that the increased thickness is due to an additional thin alkane layer on top or underneath the monolayer with the long axis of the alkanes oriented parallel to the interface.

Both, the temperature-dependent X-ray reflectivity and the diffraction measurements on submonolayer samples permitted the direct observation of the melting of the alkane monolayer. Earlier experiments in this temperature region were carried out with samples with excess alkane coverage where wetting phenomena are dominant and conceal the monolayer behavior.[19] The reflectivity and diffraction data from the submonolayer samples show clear evidence for the existence of a solid/liquid phase transition somewhere between 69.5 and 70.3 °C. This can be concluded from the disappearance of the diffraction peak and from the sudden decrease of the electron density. It also agrees with the sudden increase of the film thickness. The samples were typically covered by 90−95% with a solid alkane monolayer. Because of the substantial decrease of alkane density upon melting and because the holes in the monolayer may partially be filled with alkanes, one would expect that the all-liquid, molten alkane film is thicker than the solid monolayer at this nearly complete monolayer coverage.

Within the accuracy of the temperature measurement, the melting temperature of the alkane at submonolayer coverage, as observed with the X-ray reflectivity and diffraction, coincides with the wetting transition temperature for C30 samples at excess coverage.[19] This indicates that the wetting behavior may be linked to surface freezing. The wetting transition occurs when the spreading coefficient S defined as

$$S = \gamma_{SV} - (\gamma_{SL} + \gamma_{LV})$$

switches its sign (γ_{SV} = surface tension of the substrate/ air interface with the alkane film, γ_{SL} = surface tension

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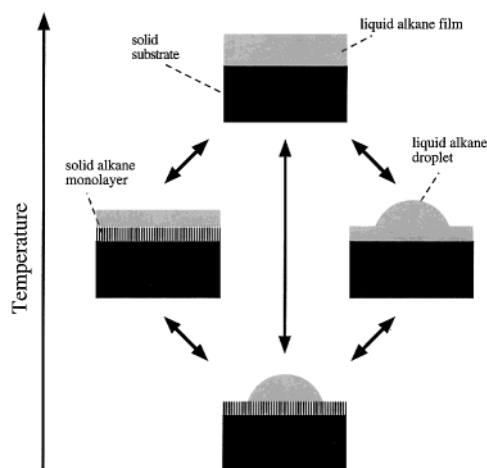
Figure 7. Schematic of conceivable scenarios for the changes in topology and in the interfacial molecular ordering at the temperature-induced wetting transition. The path in the middle shows the coupling between the wetting and surface freezing transition which is suggested from the experimental findings.

of the substrate/alkane interface, γ_{LV} = surface tension of the alkane/air interface). The spreading coefficient is a function of all three interfacial tensions. Surface freezing, on the other hand, will occur, as soon as the free energy of the alkane molecules at the solid/alkane interface is lower in their solid compared to their liquid state. It can be expected that surface freezing at the solid/alkane interface is somehow directly related to the energy of the solid/alkane interface, γ_{SL}. A relation to γ_{LV} and especially γ_{SV}, which per definition is essentially depending on the solid and vapor bulk phases (although residual alkane molecules adsorbed to the interface may affect it), is not obvious. Figure 7 shows some conceivable scenarios of the transition between the high-temperature topology and the topology in the surface freezing range. At high temperatures one observes complete wetting of an alkane film which is completely liquid. In the surface freezing temperature range one observes a liquid droplet coexisting with a solid alkane monolayer (it is not clear whether the

liquid droplet sits on the bare substrate or on the solid monolayer as it is plotted in the figure, in any case, this is not important here). The transition between the two topologies can go either via decoupled wetting and surface freezing transitions or, as the coincidence of wetting and surface freezing temperature suggests, directly with both transitions coupled (path in the middle).

Summary and Conclusion

For the first time the topology and the molecular ordering of submonolayer triacontane films at SiO_x/air interfaces has been investigated near the bulk melting temperature. Studies with three different measurement techniques—surface force microscopy, X-ray grazing incidence diffraction, and reflectivity—reveal alkane surface freezing at the SiO_x/air interface, i.e., a solidlike interfacial molecular ordering above bulk melting. To specifically focus on the behavior and molecular ordering of the interfacial alkane, the SiO_x/air interface was covered only with a molecularly thin triacontane film. Thus, contrary to earlier investigations, there was no bulk alkane whose melting and wetting behavior could interfere with the melting/solidification of the interfacial alkane layer. With surface force microscopy solid triacontane monolayer patches can be visualized above bulk melting. X-ray diffraction shows in this temperature regime a lateral molecular ordering similar to the bulk alkane rotator phase. The reflectivity data indicate that the melting temperature of the alkane monolayer coincides with the wetting transition temperature of thin bulk alkane films. The reasons and details for this coupling between wetting and melting transition are not yet understood.